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(54) Title: A METHOD TO DISPERSE NANO-CELLULOSE IN ORGANIC POLYMER PRECURSORS

(57) Abstract: This invention concerns a novel method to produce thermosets such as epoxies and polyurethanes comprising nano-cellulose. The method comprises contacting primarily water-bourne dispersed nano-cellulose with liquid thermoset precursors, specifically epoxy or amine in the case of epoxies, or glycols or similar in the case of polyurethanes. Nano-cellulose transfers to the organic phase, and water is removed at temperatures below 100 °C. Thereafter the organic phase comprising nano-cellulose can be mixed with the reactive counterpart to yield nano-composites with improved properties. The products can be used for composite articles, coatings, adhesives, sealants, and other end-uses. Preferred embodiments are described in detail.



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A METHOD TO DISPERSE NANO-CELLULOSE IN ORGANIC POLYMER PRECURSORS

FIELD OF THE INVENTION

5 The present invention relates to nano-cellulose, its dispersion in polymers and polymer precursors including epoxy and polyurethane (all in the following abbreviated as "polymers" or "polymer"), and derived products such as nano-composites, adhesives, sealants, coatings.

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BACKGROUND OF THE INVENTION

Various disclosures describe the dispersion of nano-cellulose in polymer and polymer precursors and products derived from this.

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EP2928957A1, also WO 2014/087 053, METHOD OF MANUFACTURING A NANOCELLULOSE COMPOSITE, (Kalle Nättinen, VTT Finland, publ. 2015) describes the disadvantages and problems of prior art attempts of dispersing nano-cellulose in thermoset precursors, including: a) the necessarily high water content of nano-cellulose feedstock which in turn means a high energy demand for water removal, high transport costs etc., b) the formation of crystalline segments requiring expensive filtration and removal, alternatively re-dispersion using inefficient ultrasound, and other practical problems. Said disclosure teaches the direct formation of and dispersion of pure nano-cellulose in thermoset precursors such as epoxy or hardener using efficient milling equipment. The complete process from standard cellulose to nano-composites comprising nano-cellulose is thus possible without intermediate use of water.

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CA2549844A1, SOLID PHASE DISPERSION AND PROCESSING OF MICRO- AND NANO-CELLULOSIC FIBRES IN PLASTIC PHASE TO MANUFACTURE

BIO-NANOCOMPOSITE PRODUCTS OF COMMERCIAL INTEREST (Sain Mohini M., publ 2014) discloses bio-nano-composite products using solid phase dispersion. The mechanical performance of the cellulose nanofibers is comparable to other engineering materials such as glass fibers, carbon fibers etc. In this invention a novel process for dispersion of plant stems (bundles of cellulose nanofibers with a diameter ranging between 10 to 70 nm and lengths of thousands of nanometers) has been developed to disperse cellulosic microfibrils and nanofibrils in solid phase into a molten plastic matrix or in a low viscosity water-based resin system in aqueous phase. The invention relates to manufacturing Bio-nanocomposites of high performance by dispersing micro-and nano-cellulosic fibres into plastic matrix using conventional plastic processing equipment. This invention also overcomes one unique challenge of bio-nanocomposite processing, which is to make them commercially viable by surface modifying cellulosic micro-and nano-fibrils derived from renewable resources.

US20160115359A1, WOOD ADHESIVES CONTAINING REINFORCED ADDITIVES FOR STRUCTURAL ENGINEERING PRODUCTS (Wang, Siqun, Univ. of Tennessee, publ. 2016) describes wood adhesives possibly including nano-cellulose, however, the disclosure is silent about special dispersion methods.

Not directly relevant, but interesting prior art includes US9376503, Cellulose-based composite materials (Shoseyov, Oded, publ 2016), which discloses a composite article, comprising a scaffold arranged in substantially ordered nanosheets and having a plurality of pores, the scaffold comprising at least one cellulose nano-material selected from the group consisting of ... cellulose; and at least one polymer

resin at least partially occupying a plurality of pores in the scaffold.

OBJECT OF THE INVENTION

5 The object of the invention is to produce thermosets comprising nano-cellulose.

A further object of the invention is to provide thermosets comprising well dispersed nano-cellulose.

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A further object of the invention is to provide thermosets with improved properties such as increased impact resistance, increased tensile strength, and improved adhesion to various substrates.

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A further object of the invention is to provide a method of preparing thermosets which is energy-efficient, economic and scalable.

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A further object of the invention is to use the thermosets as composite articles, coatings, adhesives, sealants, and other end-uses.

SUMMARY OF THE INVENTION

25 The objects of the invention are attained by the method to produce thermosets including epoxies and polyurethanes.

In a preferred embodiment of the invention, the method to produce thermosets including epoxies and polyurethanes comprising
30 0.1-10 % by weight nano-cellulose, comprises the following steps:

- a) nano-cellulose is provided as water-bourne dispersion, optionally containing up to 50% ethanol, whereby said

dispersion comprises at least 0.2%, preferably at least 0.3%, most preferably about 2-5% by weight nano-cellulose,

b) said nano-cellulose is intensively mixed with an organic phase, specifically a thermoset precursor selected from epoxy, epoxy hardener, glycol and/or polyol,

c) upon transfer of nano-cellulose to the organic phase, water and said optional ethanol are removed by distillation at a temperature below 100 °C for minimising loss of reactive functionality of epoxy or polyurethane,

d) the dry organic phase comprising nano-cellulose is mixed with the appropriate amount of reactive counterpart and optionally other desired additives, wherein said reactive counterpart is amine hardener for epoxies, and wherein said reactive counterpart is glycol or amine for polyisocyanate, and

e) the final product is achieved following known curing procedures,

said method **further characterized** by the fact that loss of reactive functionality of epoxy or polyurethane due to reaction with water is limited to < 50% of reactive epoxy or polyurethane, preferably < 20% or < 10% or <5% of reactive epoxy or polyurethane.

In a further preferred embodiment of the method, said distillation is by speed distillation, preferably high-speed distillation.

In a further preferred embodiment of the method, said distillation is by using a rotary evaporator and/or wiped film evaporator.

In a further preferred embodiment of the method, said distillation is by using a rotary evaporator.

5 In a further preferred embodiment of the method, said distillation is by using a wiped film evaporator.

In a further preferred embodiment of the method, said distillation is by using an extruder, including a planetary extruder with possibility for gas removal.

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In a further preferred embodiment of the method, said nanocellulose is microfibrillar cellulose (MFC) and/or nanocrystalline cellulose (NCC).

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In a further preferred embodiment of the method, said nanocellulose is selected from and shall be understood as cellulosic fibres, in particular cellulosic fibres obtained by defiberizing of lignocellulosic raw-material, optionally bleached, with typical fiber lengths of 10 nanometer up to 100 micrometer, also comprising nanocrystalline cellulose (NCC) and microfibrillar cellulose (MFC).

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In a further preferred embodiment of the method, said epoxy compounds are selected from organic compounds carrying at least two epoxy functionalities, including bisphenol A adducts with epichlorohydrin.

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In a further preferred embodiment of the method, the residual water content in the polymer (e.g. epoxy) / cellulose mixture is reduced to below 10% by weight, preferably to below 3% and even more preferably to below 1% by treatment in a rotary evaporator, in a wiped-film-evaporator or in an extruder with

possibility for gas removal, ideally under a pressure below 1 bar.

In a further preferred embodiment of the method, carbon nano
5 tubes (CNT) are part of the composition, and where CNT may be
dispersed e.g. by ultrasound separately in water and mixed
thereafter with water/cellulose, or where CNT are dispersed in
presence of cellulose, and where the final content of CNT in
finished products may range from 0.1% by weight to 10% by
10 weight,

In a further preferred embodiment of the method, the loss of
reactive functionality of epoxy or polyurethane due to reac-
tion with water is compensated by adjusting the hardener reac-
15 tion during curing, or by adding additional epoxy or diisocya-
nate to ensure complete cross-linking, including reaction of
e.g. diols formed by reaction of epoxy and water.

The objects of the invention are also attained by a composi-
20 tion produced according to the above mentioned preferred em-
bodiments of the method.

In a preferred embodiment, the composition comprises nano-cel-
lulose and polymer selected from epoxy, epoxy hardener or pol-
25 yurethane hardener such as glycol, optionally containing car-
bon nano tubes and other functional additives including
defoamers, pigments, antioxidants, viscosity adjusting chemi-
cals and resins for adhesives.

The objects of the invention are also attained by an article
30 such as a composite article, a coating, an adhesive or a seal-
ant based on the above mentioned preferred embodiments of the
composition.

The objects of the invention are also attained by use of a composition according the above mentioned preferred embodiment of the composition as a composite article, a coating, an adhesive or a sealant.

DETAILED DESCRIPTION

In one aspect, the invention describes improved methods to produce thermosets including epoxies and polyurethanes comprising 0.1-10 % by weight nano-cellulose, comprising the following steps:

- a) nano-cellulose is provided as water-bourne dispersion, optionally containing up to 50% ethanol, whereby said dispersion comprises 0.2-10% by weight, preferably 0.3-5% nano-cellulose,
- b) said nano-cellulose is intensively mixed with an organic phase, specifically a thermoset precursor selected from epoxy, epoxy hardener, glycol and/or polyol,
- c) upon transfer of nano-cellulose to the organic phase, water is removed by distillation at a temperature below 100 °C,
- d) the dry organic phase comprising nano-cellulose is mixed with the appropriate amount of reactive counterpart (epoxy - amine hardener; polyisocyanate - glycol or amine) and optionally other desired additives,
- e) the final product is achieved following known curing procedures.

In another aspect of the invention, the function of various additives such as carbon nano tubes (CNT) for imparting e.g. electrical conductivity or microwave absorbancy, additional epoxy to guarantee cross-linking of side reaction products such as diols from the reaction of epoxy with water, and other additives is disclosed.

In comparison to prior art, the invention succeeds in providing thermosets comprising well dispersed nano-cellulose with improved properties such as increased impact resistance, increased tensile strength, and improved adhesion to various
5 substrates. The methods disclosed are energy-efficient, economic and scalable.

In the present invention, nano-cellulose shall be understood as cellulosic fibres, in particular cellulosic fibres obtained by defibering of lignocellulosic raw-material, optionally
10 bleached, with typical fiber lengths of 10 nanometer up to 100 micrometer, also comprising nanocrystalline cellulose (NCC) and microfibrillar cellulose (MFC).

In the present invention, epoxy is defined as a raw material
15 for epoxy composites, typically comprising bisphenol-A, bisphenol-F and related di- or polyfunctional compounds comprising epoxy groups (-CH₂-COH₂-) where the oxygen atom O and the two carbon atoms C form a reactive ring structure, said epoxy typically reacted with amines or other hardeners to cross-
20 linked thermosets.

EXAMPLES

Methods and compositions and finished products are described in the following section. Those are useful for the production
25 of goods such as composites, coatings, adhesives and sealants.

Example 1

Low molecular weight epoxy types (bis A/F) such as epikote 235 were used in example 1. These are reaction products of CAS:
30 25068-38-6 NLP: 500-033-5 reg. nr. : 01-2119456619-26-0006, bisfenol-A and epichlorohydrin 50-100%, CAS: 9003-36-5 NLP:

500-006-8, reg nr: 01-2119454392-40-0003, Formaldehyde, oligo-
meric reaction products with 1-chloro-2,3-epoxypropane and
phenol 25-50%,

Viscosity: 6-8000 mPas, epoxy equivalent 175 - 185.

5

Epoxy and MFC were mixed and dispersed for 30 min at 3000 rpm
using a Dispermill Yellow-Line dissolver. Residual water was
removed by a) heating the mixture overnight in an oven at ca.
80 °C, b) by using a rotary evaporator, with vacuum at 40 °C,
10 c) by using a wiped film evaporator under vacuum, d) by using
an extruder with gas outlets for water removal. Reference sam-
ples were prepared by mixing with water without nano- or mi-
crofibrillar cellulose.

15

The reaction of epoxy with water yielding a diol is the most
significant loss reaction. The reaction of epoxy with OH
groups in cellulose was found to be slow. It turned out that
wiped film evaporation and extrusion with gas removal are ef-
ficient at minimizing the side reaction(s). Reduced effective
20 epoxy content can be compensated in two ways, a) reducing the
hardener amount by 2-20% to afford complete reaction between
epoxy and (amine) hardener, b) adding additional epoxy to af-
ford reaction between diols and excess epoxy. The latter
method results in stronger composites.

25

The final water content can approach zero, but for practical
purposes about 1% water by weight or up to 3% is acceptable
for most products.

30

Example 2

NFC and MFC were dispersed in water-soluble amines, partly wa-
ter-soluble amines, amides as well as glycols as precursors

for polyurethanes. It was not attempted to disperse cellulose in isocyanates as these chemicals react too fast with water. Curing of epoxy or diisocyanate with above mentioned hardener / cellulose mixtures proceeds as without cellulose addition, however, for water-soluble amines a shortened hardening time or pot life was observed.

Example 3

Carbon nano tubes (CNT) were dispersed in water using ultrasound using known procedures. Dispersed CNT were added to nano-cellulose in water, and the mixture was further dispersed in order to afford complexes of CNT and nano-cellulose. (CNT can also directly be treated with ultrasound in the cellulose-water mixture, however, the cellulose is exposed to high temperatures in that case.) Mixing said CNT/cellulose blend with epoxy results in a faster phase transfer of CNT/cellulose into epoxy compared with the phase transfer rate of pure cellulose. This is possibly due to the increased hydrophobicity of the CNT/cellulose complex. Following the general procedure outlined in example 1, products result characterized by increased electrical conductivity and microwave absorbance. The weight ratio CNT / cellulose can be varied widely, e.g. between 5:95 to 95:5, but a 30:70 to 70:30 weight ratio is preferred. The total CNT content in the final formulation may be 0,1-10% or higher by weight where conductivity increases with increasing CNT content.

Example 4

The following table discloses a useful formulation for an anti-corrosive coating:

Epoxy Primer Oxide Red			
A-component			
Raw material	Wt%	Density	Volume
Bis A/F-Ep resin	32	1.13	28.61
MFC-3%	6	1.1	5.87
<i>Mix for 5 min. Add:</i>			
Defoamer	1	0.8	1.21
Flow additive	0.5	0.97	0.45
<i>Mix 2-3 min. Add:</i>			
Red iron oxide	16	5	3.23
Fumed silica	3.5	2.2	1.47
Plastorit	8	2.9	2.79
<i>Grind</i>			
Bis A/F-Ep resin	33	1.13	28.61
Sum	100	1.38	72.25
B-component			
Raw material	Wt%	Density	Volume
Polyaminoamide CA	24	1.01	71.57
Cycloaliphatic CA	9	0.92	30.12
Sum	33	0.98	101.69

Useful formulations for composites, adhesives and the like follow known art except for 2-10% increased epoxy addition, to compensate for epoxy loss due to reaction with water.

5 Material properties: as discussed above, it was found that the speed of water removal from epoxy/nano-cellulose is important to minimize the epoxy-to-diol loss reaction. In fact, simple overnight removal of water in an oven converts an estimated 50% of epoxy to diol, finally resulting in a composite with
10 reduced impact strength compared to a formulation not containing any nano-cellulose. Wiped film evaporation reduces the loss reaction to about 10% or less, depending on the combination of temperature and vacuum. For such formulations, impact strength was increased by 10% and more even without further
15 optimisation by e.g. adjusting the epoxy concentration to match the hardener concentration. The same trend is observed for adhesion, cohesive strength, tensile strength and other mechanical properties.

CLAIMS

1. A method to produce thermosets including epoxies and polyurethanes comprising 0.1-10 % by weight nano-cellulose, comprising the following steps:

- 5 a) nano-cellulose is provided as water-bourne dispersion, optionally containing up to 50% ethanol, whereby said dispersion comprises at least 0.2%, preferably at least 0.3%, most preferably about 2-5% by weight nano-cellulose,
- 10 b) said nano-cellulose is intensively mixed with an organic phase, specifically a thermoset precursor selected from epoxy, epoxy hardener, glycol and/or polyol,
- c) upon transfer of nano-cellulose to the organic phase, water and said optional ethanol are removed by distillation at a temperature below 100 °C for minimising loss of
- 15 reactive functionality of epoxy or polyurethane,
- d) the dry organic phase comprising nano-cellulose is mixed with the appropriate amount of reactive counterpart and optionally other desired additives, wherein said re-
- 20 active counterpart is amine hardener for epoxies, and wherein said reactive counterpart is glycol or amine for polyisocyanate, and
- e) the final product is achieved following known curing procedures,

25 said method **further characterized** by the fact that loss of reactive functionality of epoxy or polyurethane due to reaction with water is limited to < 50% of reactive epoxy or polyurethane, preferably < 20% or < 10% or <5% of reactive epoxy or

30 polyurethane.

2. The method according to claim 1 wherein said distillation is by speed distillation, preferably high-speed distillation.

3. The method according to claim 1 or 2 wherein said distillation is by using a rotary evaporator and/or wiped film evaporator.

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4. The method according to any one of the preceding claims wherein said distillation is by using a rotary evaporator.

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5. The method according to any one of the preceding claims wherein said distillation is by using a wiped film evaporator.

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6. The method according to any one of the preceding claims wherein said distillation is by using an extruder, including a planetary extruder with possibility for gas removal.

7. The method according to any one of the preceding claims wherein nano-cellulose is microfibrillar cellulose (MFC) and/or nanocrystalline cellulose (NCC).

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8. The method according to any one of the preceding claims where nano-cellulose is selected from and shall be understood as cellulosic fibres, in particular cellulosic fibres obtained by defibering of lignocellulosic raw-material, optionally bleached, with typical fiber lengths of 10 nanometer up to 100 micrometer, also comprising nanocrystalline cellulose (NCC) and microfibrillar cellulose (MFC).

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9. The method according to any one of the preceding claims where epoxy compounds are selected from organic compounds carrying at least two epoxy functionalities, including bisphenol A adducts with epichlorohydrin,

10. The method according to one of the preceding claims where the residual water content in the polymer (e.g. epoxy) / cellulose mixture is reduced to below 10% by weight, preferably to below 3% and even more preferably to below 1% by treatment
5 in a rotary evaporator, in a wiped-film-evaporator or in an extruder with possibility for gas removal, ideally under a pressure below 1 bar.

11. The method according to one of the preceding claims where
10 carbon nano tubes (CNT) are part of the composition, and where CNT may be dispersed e.g. by ultrasound separately in water and mixed thereafter with water/cellulose, or where CNT are dispersed in presence of cellulose, and where the final content of CNT in finished products may typically range from 0.1%
15 by weight to 5 or 10 % by weight.

12. The method according to one of the preceding claims where loss of reactive functionality of epoxy or polyurethane due to reaction with water is compensated by adjusting the hardener
20 reaction during curing, or by adding additional epoxy or diisocyanate to ensure complete cross-linking, including reaction of e.g. diols formed by reaction of epoxy and water.

13. A composition produced according to the method in one of
25 the preceding claims comprising nano-cellulose and polymer selected from epoxy, epoxy hardener or polyurethane hardener such as glycol, optionally containing carbon nano tubes and other functional additives including defoamers, pigments, antioxidants, viscosity adjusting chemicals and resins for adhesives.
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14. An article such as a composite article, a coating, an adhesive or a sealant based on a composition according to claim 12.

5 15. Use of a composition according to claim 13 as a composite article, a coating, an adhesive or a sealant.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/053587

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J3/20 C08J3/205 C08J5/00 C08J3/24 C08L1/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C08J C08L
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/087053 A1 (TEKNOLOGIAN TUTKIMUSKESKUS VTT [FI]) 12 June 2014 (2014-06-12)	13-15
A	page 1, line 1 - page 9, last line; claims 1-16	1-12
X	CA 2 549 844 A1 (SAIN MOHINI M [CA]) 25 November 2007 (2007-11-25)	13-15
A	cited in the application page 1, line 1 - page 2, last line	1-12
X	US 2016/115359 A1 (WANG SIQUN [US] ET AL) 28 April 2016 (2016-04-28)	13-15
A	cited in the application paragraphs [0001] - [0126]; claims 1-17	1-12
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ansorge, Markus
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/053587

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/007163 A1 (NANOCYL SA [BE]; UNIV LEUVEN KATH [BE]; MEZZO LUCA [IT]; GODARA AJAY []) 21 January 2010 (2010-01-21) abstract; claims 1-11 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2018/053587

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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